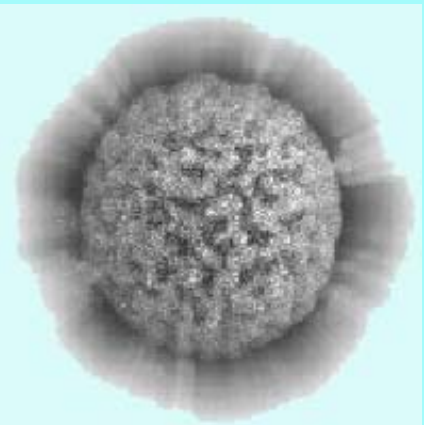
ECS meeting, Salt Lake City, 2002

Combinatorial Synthesis of Oxygen Reduction Electrocatalysts by Spray Pyrolysis



Paul Napolitano, David Dericotte, Rimple Bhatia, Paolina Atanassova, Mark Hampden-Smith, Toivo Kodas

SUPERIOR MicroPowders

Contents

- SMP powder manufacturing platform
- Combinatorial discovery approach
  - » Combinatorial system design
  - » Choice, synthesis, characterization and testing of electrocatalysts
  - » MEA structure development
- Benchmark synthesis of binary and ternary alloy ORR catalysts

SUPERIOR MicroPowders

Challenges for Combinatorial Discovery

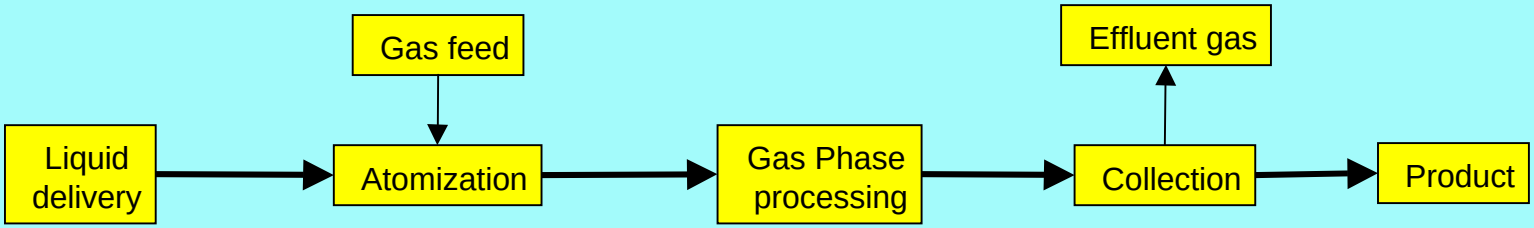
- *The goal of combinatorial discovery is to screen as many materials or properties as possible in a short time = many small size samples*
- *Discover the materials on the system that will be used for high volume manufacturing to produce the same material highly reproducibly*
- *Does the microstructure and composition really represent what can be reproduced at a commercial scale?*
- *Use a powder production system that is sufficiently flexible to reproduce discovered compositions*

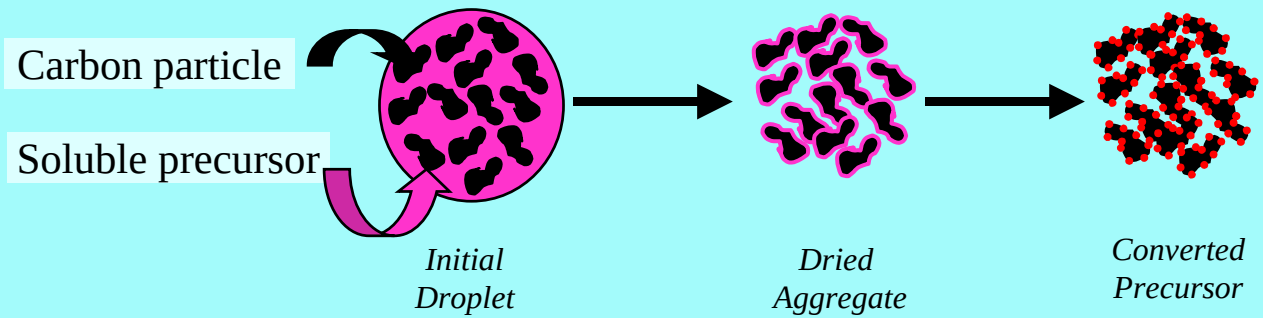
Technology Platform: SMP's Spray Based Manufacturing

- Low cost manufacturing
  - » Single step processing
  - » Highly controllable and reproducible
  - » "Green" process with minimal waste streams
- Agile platform
  - » Not material specific
  - » Inorganics, organics, metals, metal oxides
  - » Complex compositions
- Ability to engineer critical properties
  - » Particle morphologies and size distributions
  - » Bulk and surface chemistries and structures
  - » Dispersion, crystallinity and size distribution of catalytically active phase

SUPERIOR MicroPowders

Technology Platform: Process Flow Diagram

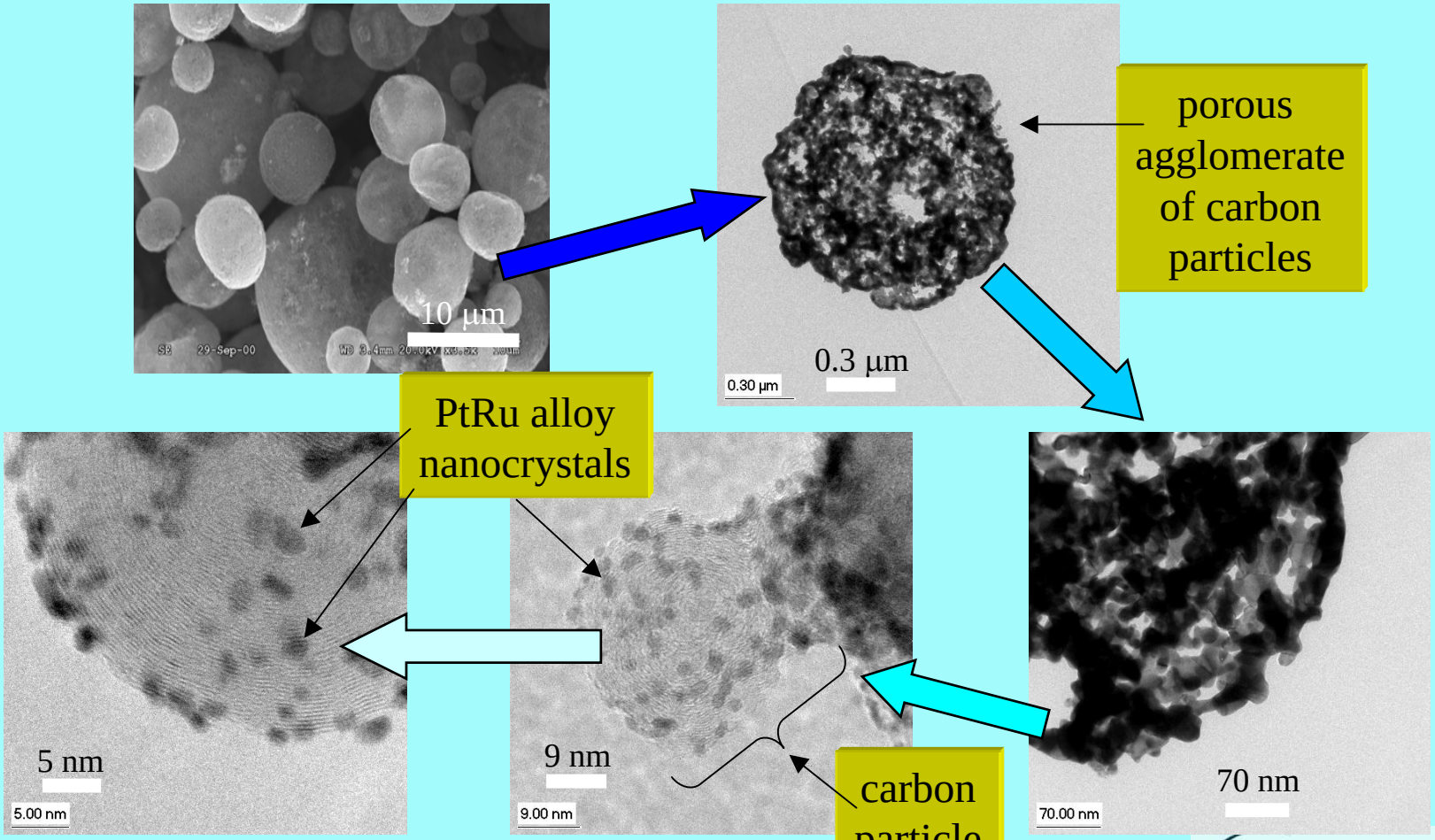




- Independent control over:
  - » aggregate morphology and size distribution
  - » the dispersion and composition of catalytically active phase

SUPERIOR MicroPowders

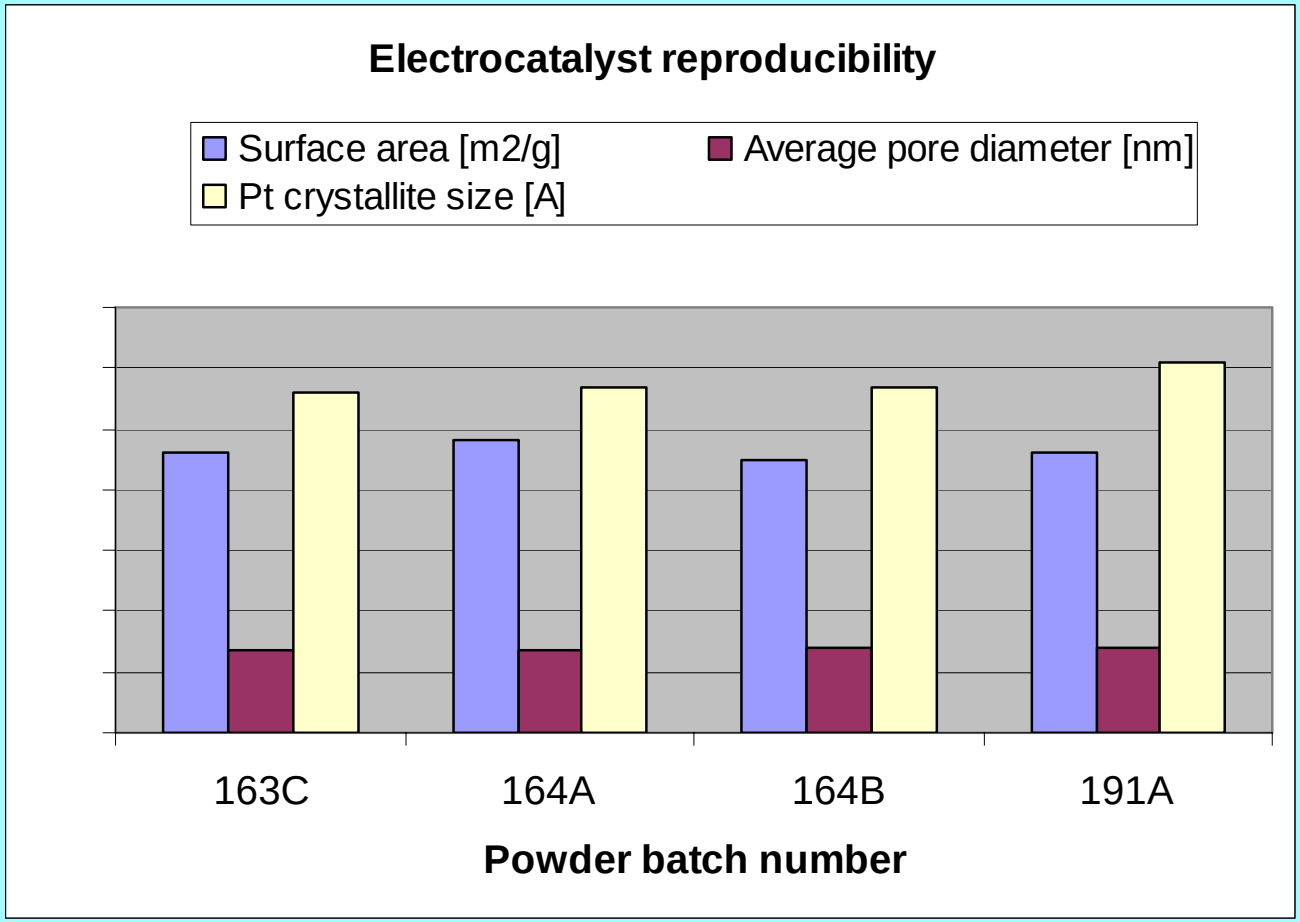
Hierarchical Structure of SMP Electrocatalyst



Relevant patents: US 6,103,393 US 6,165247 US 6,159,267

SUPERIOR MicroPowders

Simultaneous Structure Control



- Scale up reproducibility
- Batch-to-batch reproducibility
- Sub-batch reproducibility

SUPERIOR MicroPowders

From Combinatorial Discovery to Production

Production
1,000's Kg
range

Pilot
Kgs range

Research
100g range

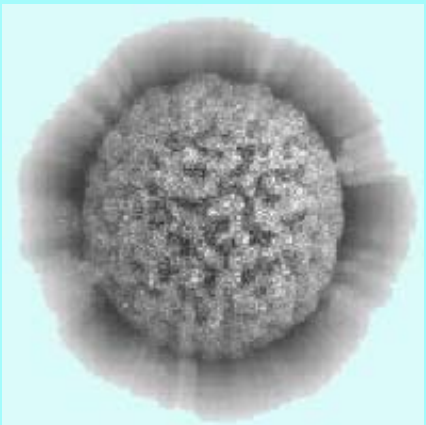
SUPERIOR MicroPowders

SMP DOE Program

Title of Project: *Development of High-Performance, Low-Pt Cathodes Containing New Catalysts and Layer Structure*

Duration: *4 years, September 2001- September 2005*

DOE Program Manager: *JoAnn Milliken*

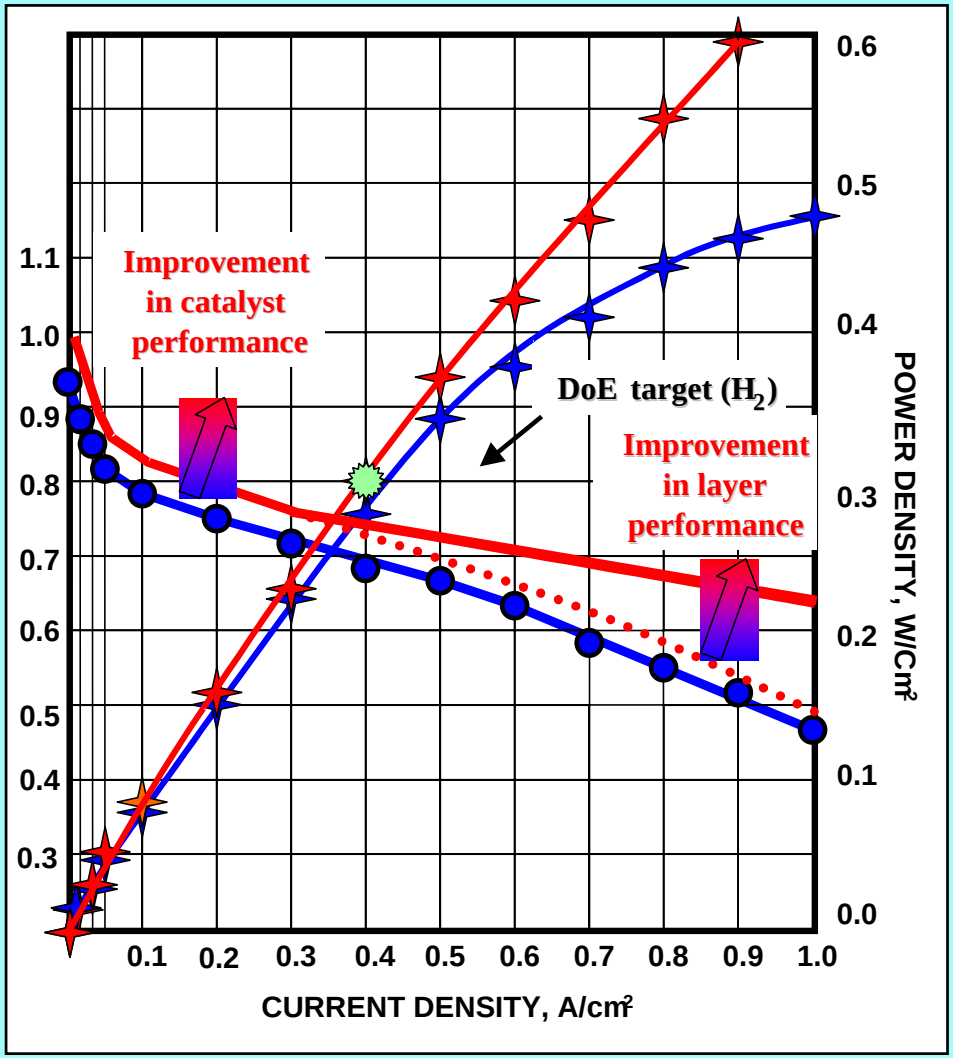


Subcontractors: *DuPont*
CFDRC

Stack testing: *GM*

SUPERIOR MicroPowders

Technical Goals and Objectives



- Current state of the art:
  - 2002 - 2 gPt/kW at 0.8 V; > 1000 h
    0.65 mg Pt/cm² loading
  - recent reports - 1gPt/kW
- DOE target performance:
  - 2004 - 0.6 gPt/kW at 0.8 V; > 4000 h
    0.20 mg Pt/cm² loading
  - 2008 - 0.2 gPt/kW at 0.8 V; > 5000 h
    0.05 mg Pt/cm² loading

SUPERIOR MicroPowders

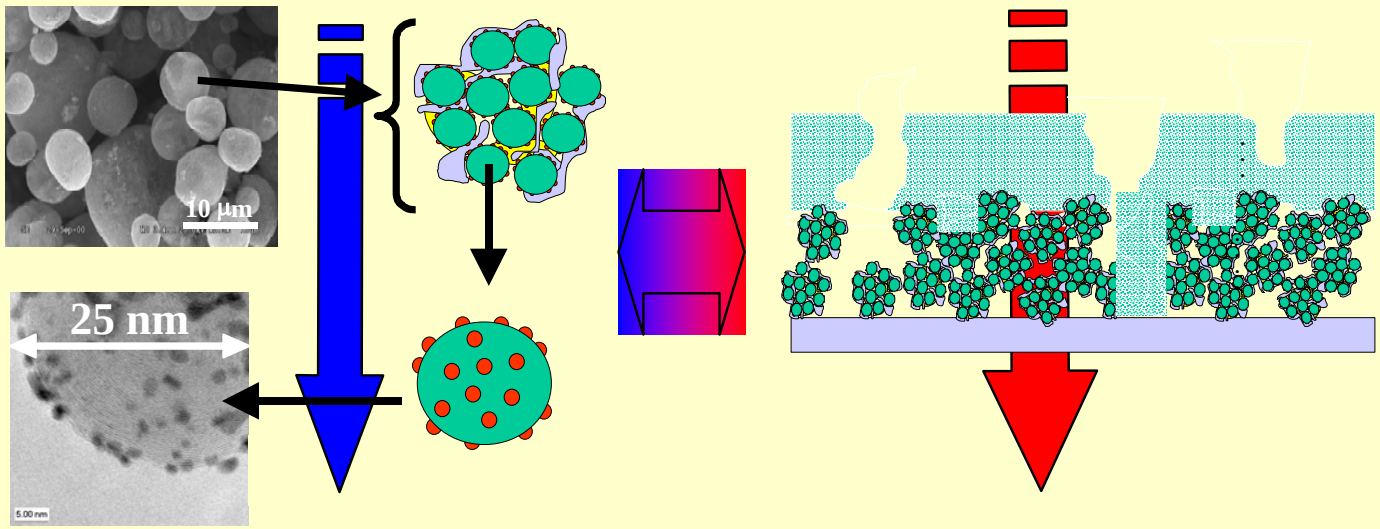
Technical Concept

Effort 1

Discovery of new, low Pt catalyst compositions and particle microstructures

Effort 2

Modeling and deposition of engineered cathode layers

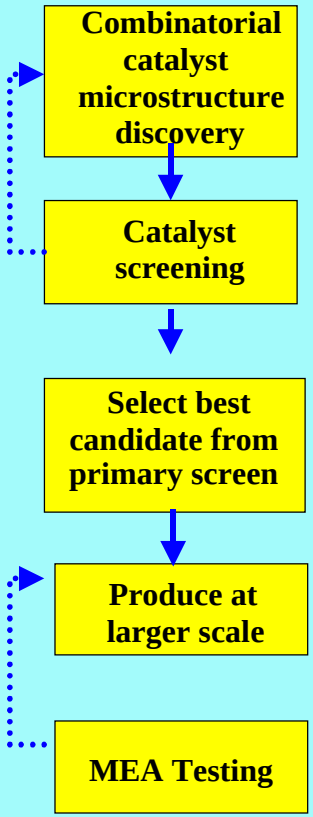


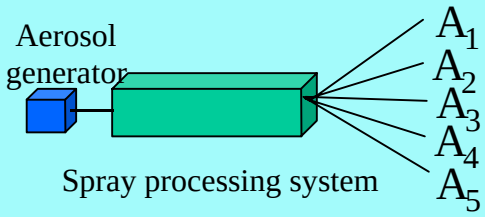
High Performance Low-Cost MEA

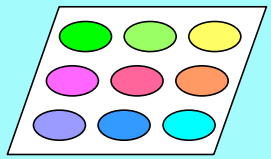
- Effort 1:
  - *SMP*
  - *DuPont*
- Effort 2:
  - *SMP/*
  - *CFDRC*
- Short Stack Testing:
  - *GM*

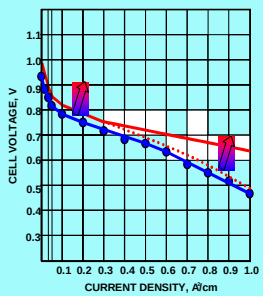
SUPERIOR MicroPowders

Work Plan Effort 1: Combinatorial Approach









- ***Combinatorial Powder Synthesis System (CPSS) - SMP***
  - » Synthesis of Binary Alloys and Mixed Metal/Metal Oxides
  - » Synthesis of Ternary Alloys
- ***Rapid Catalyst Screening for ORR Activity - DuPont***

SUPERIOR MicroPowders

Combinatorial Approach for Electrocatalyst Discovery

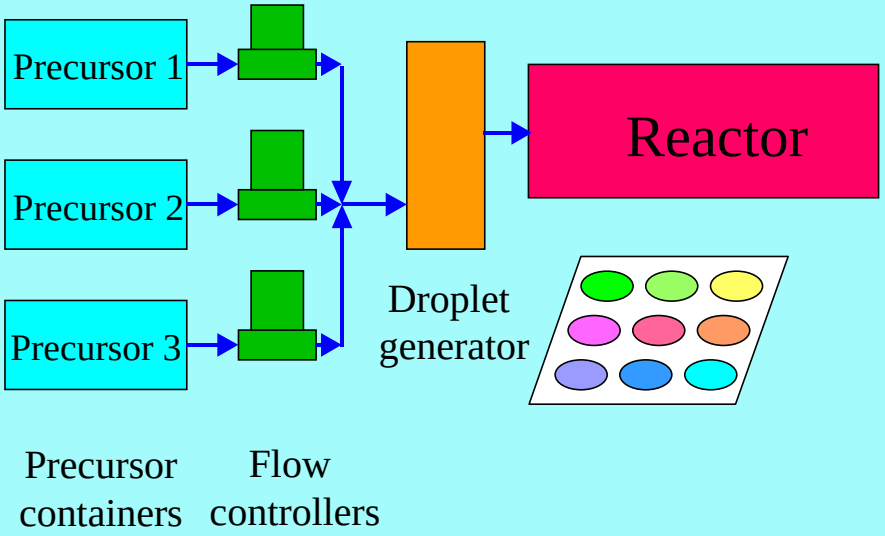
- SMP combinatorial discovery platform:
  - » Fully automated powder production
  - » Compatible with scaled manufacturing
- Critical elements of the approach:
  - » Some combinatorial platforms rely on high throughput techniques for model systems followed by scale up in supported form
  - » SMP approach will rely on fewer carefully chosen compositions made in supported form
  - » Screening focused on test configurations such as half cell and MEA configurations)

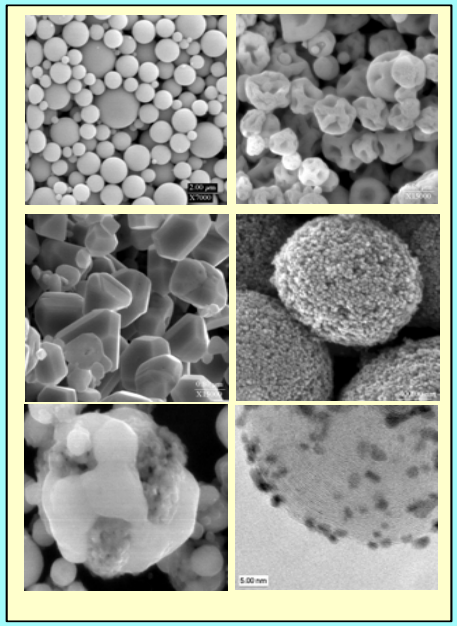
SUPERIOR MicroPowders

Components of Combinatorial Approach

- ***Selection of composition/structure targets*** and benchmarking against literature/existing catalysts
- Ensure ***high speed generation of samples*** with variations in the composition and microstructure: an order of magnitude higher number of samples
- Ensure ***rapid primary screens*** to evaluate structure/performance of electrocatalyst powders:
  - » XRD for structure evaluation (crystallinity, dispersion, alloying)
  - » rapid EC performance evaluation in half cell configuration

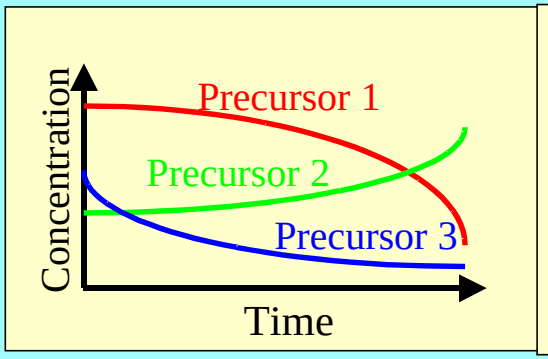
Combinatorial Powder Synthesis System (CPSS)



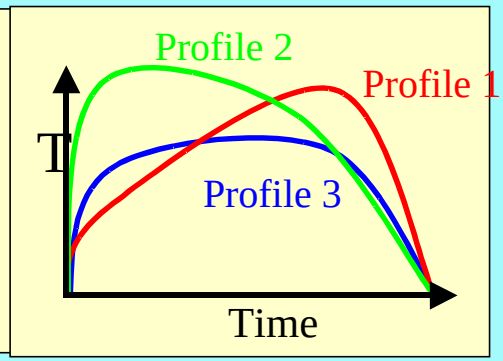


- Surface area
- Dispersion
- Composition
- Crystallinity
- Phase
- Surface composition
- Morphology
- Porosity
- Pore structure
- Particle size & distribution

Composition



Microstructure



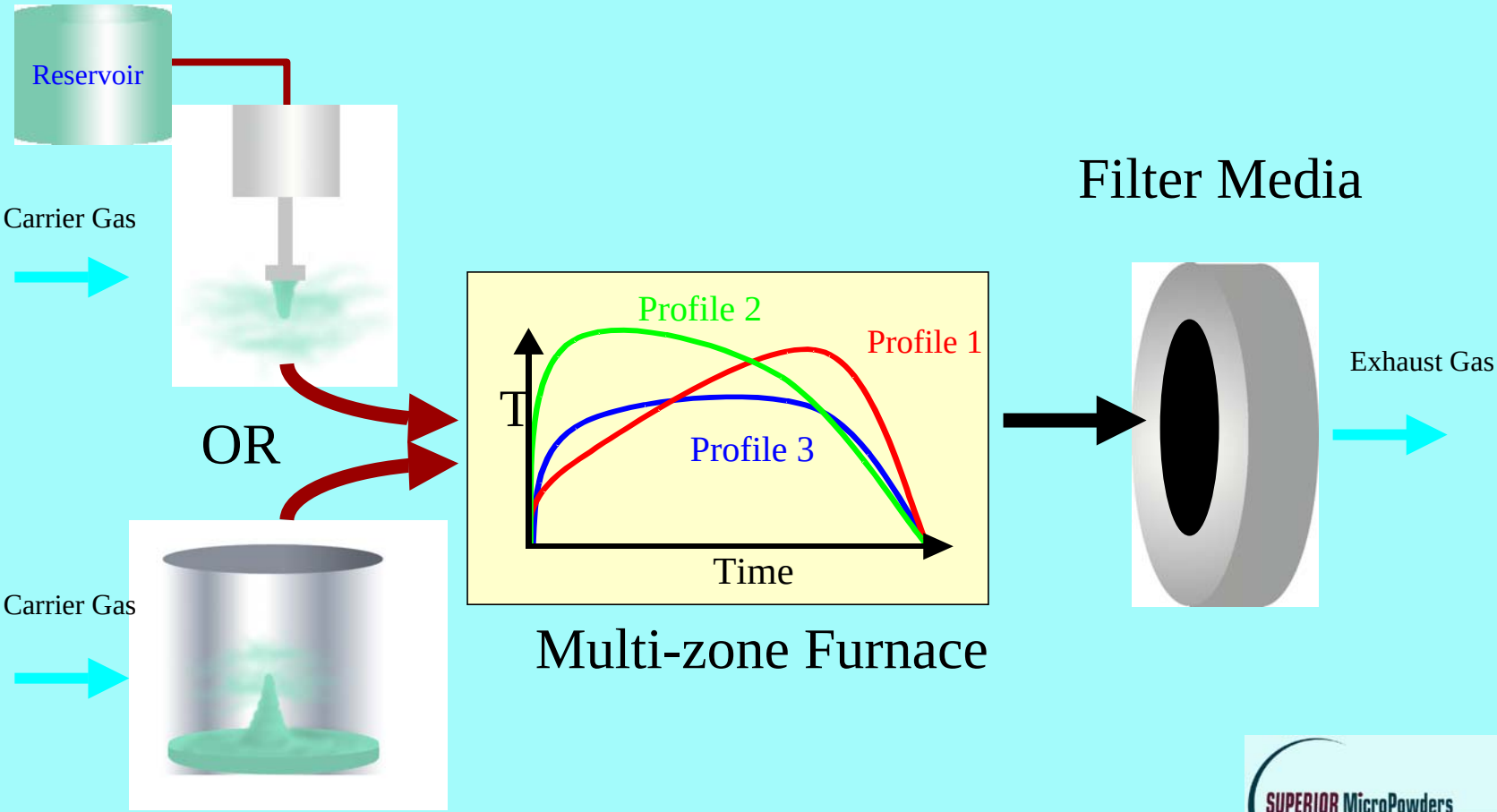
SUPERIOR MicroPowders

SMP Powder Production Process

Atomization Zone

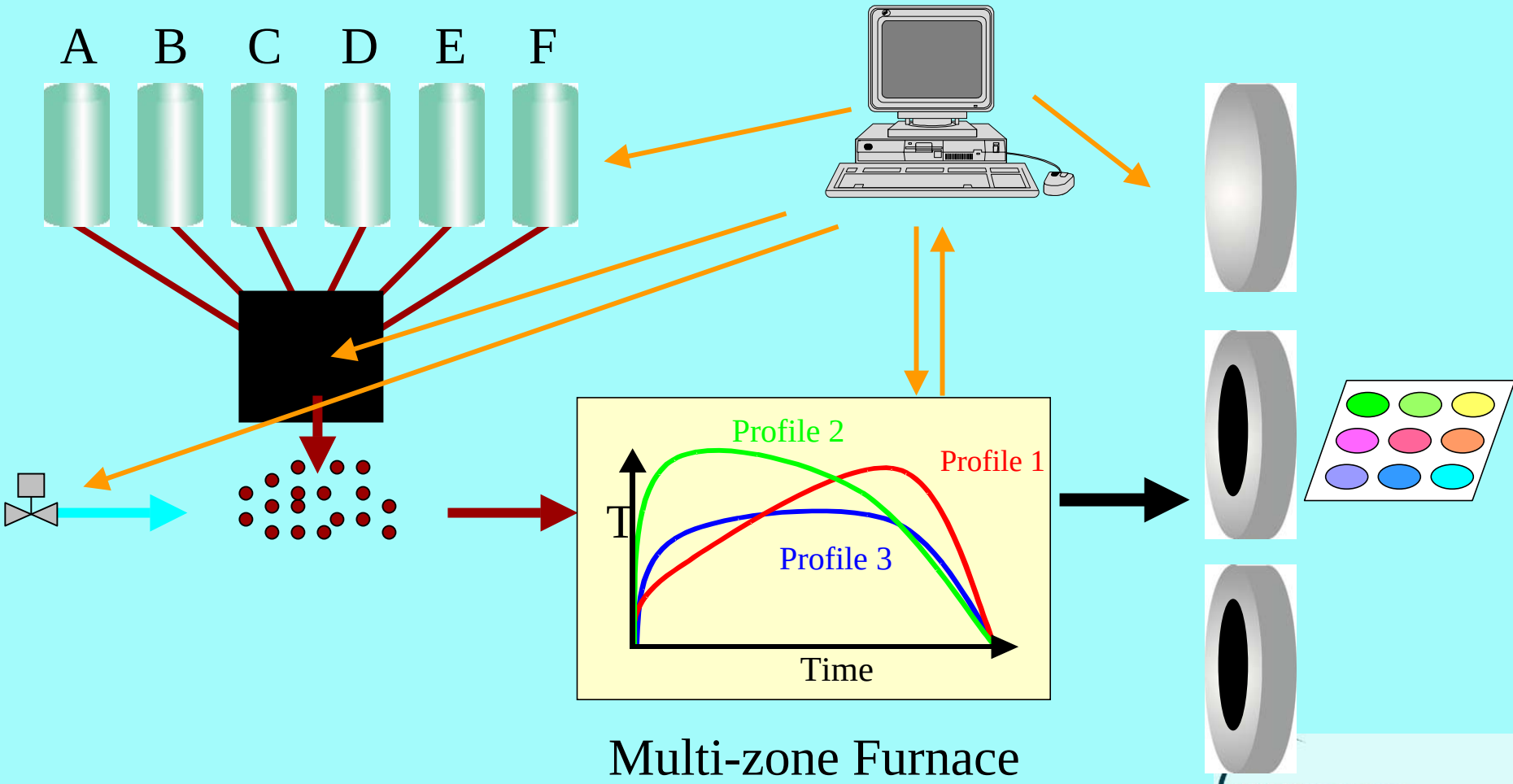
Reaction Zone

Collection Zone



SUPERIOR MicroPowders

Process Automation



Multi-zone Furnace

SUPERIOR MicroPowders

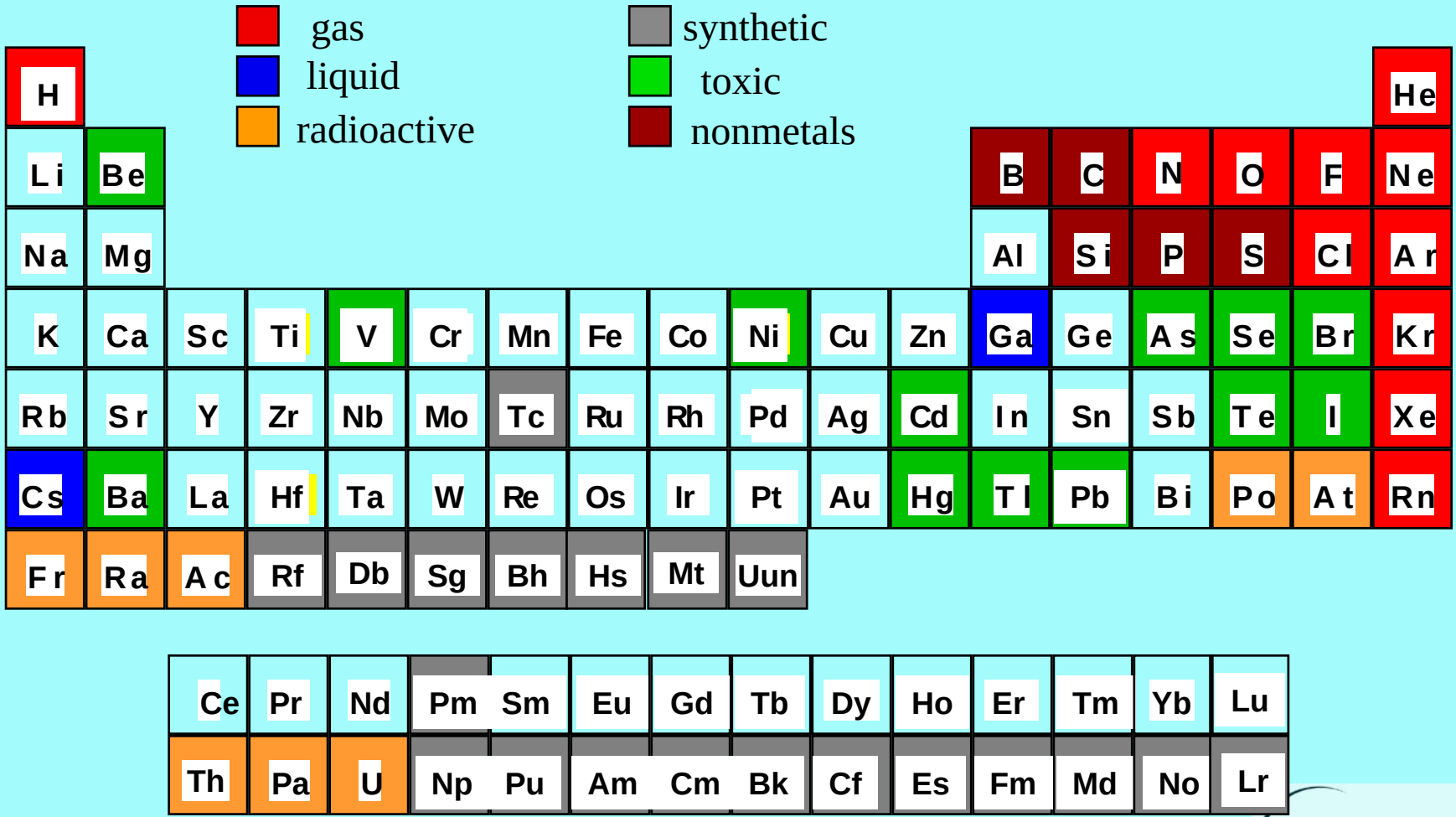
Automation and Upgrades

Process Step	*Current Limitation*	*Modification*
Precursor delivery	➢Static precursor composition	➢Automate delivery ➢Add "on-the-fly" preparation
Automation	➢Operator required to: ▪adjust furnace temp ▪adjust gas flow rate ▪replace collection media	➢Automate system to: ▪adjust furnace temp ▪adjust gas flow rate ▪isolate powder sample
Data Collection	➢Limited data collection performed by operator	➢Use SCADA to acquire more data, control process variables, perform statistical analysis
Safety	➢Safety systems installed to protect operator, system and powder	➢Improve further safety controls

Selection of Composition/ Structure Targets

- ***Selection criteria for electrocatalyst compositions:***
  - » Cost of components - raw materials, precursor cost
  - » Cost of manufacturing (precursors, processing steps) - fab cost
  - » Demonstrated performance advantage
  - » Possible performance advantage based on established general trends
  - » Long term stability
    - – stable in acidic media/resistant to corrosion
    - – sustainable performance at high potentials
    - – sustainable dispersion of the active phase
- ***Demonstrate synthesis of complex known compositions and benchmark performance***
- ***Develop methodology to down select in the compositional space***

Selection of Composition Targets

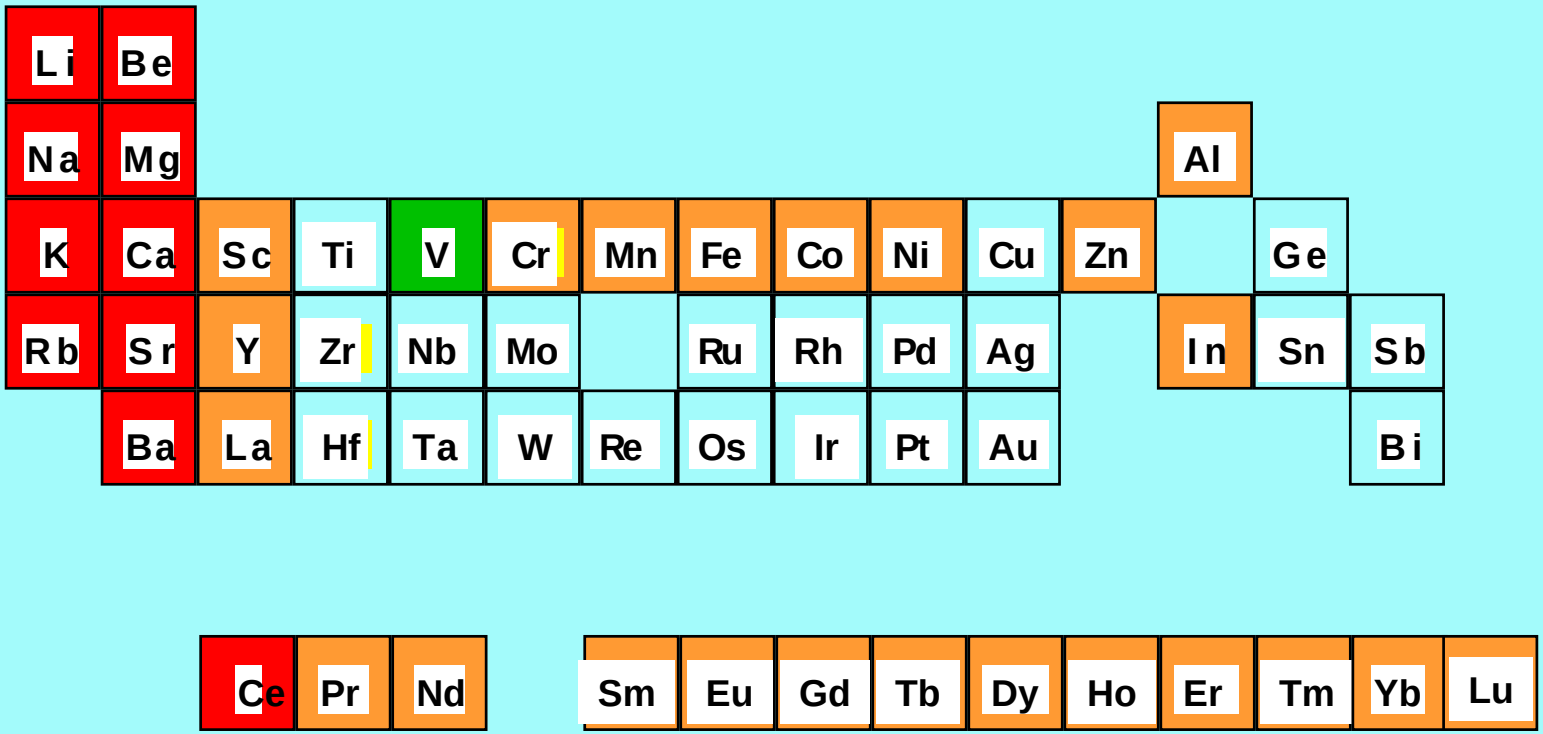


SUPERIOR MicroPowders

Selection of Composition Targets for Binary Metal-Metal Oxide EC

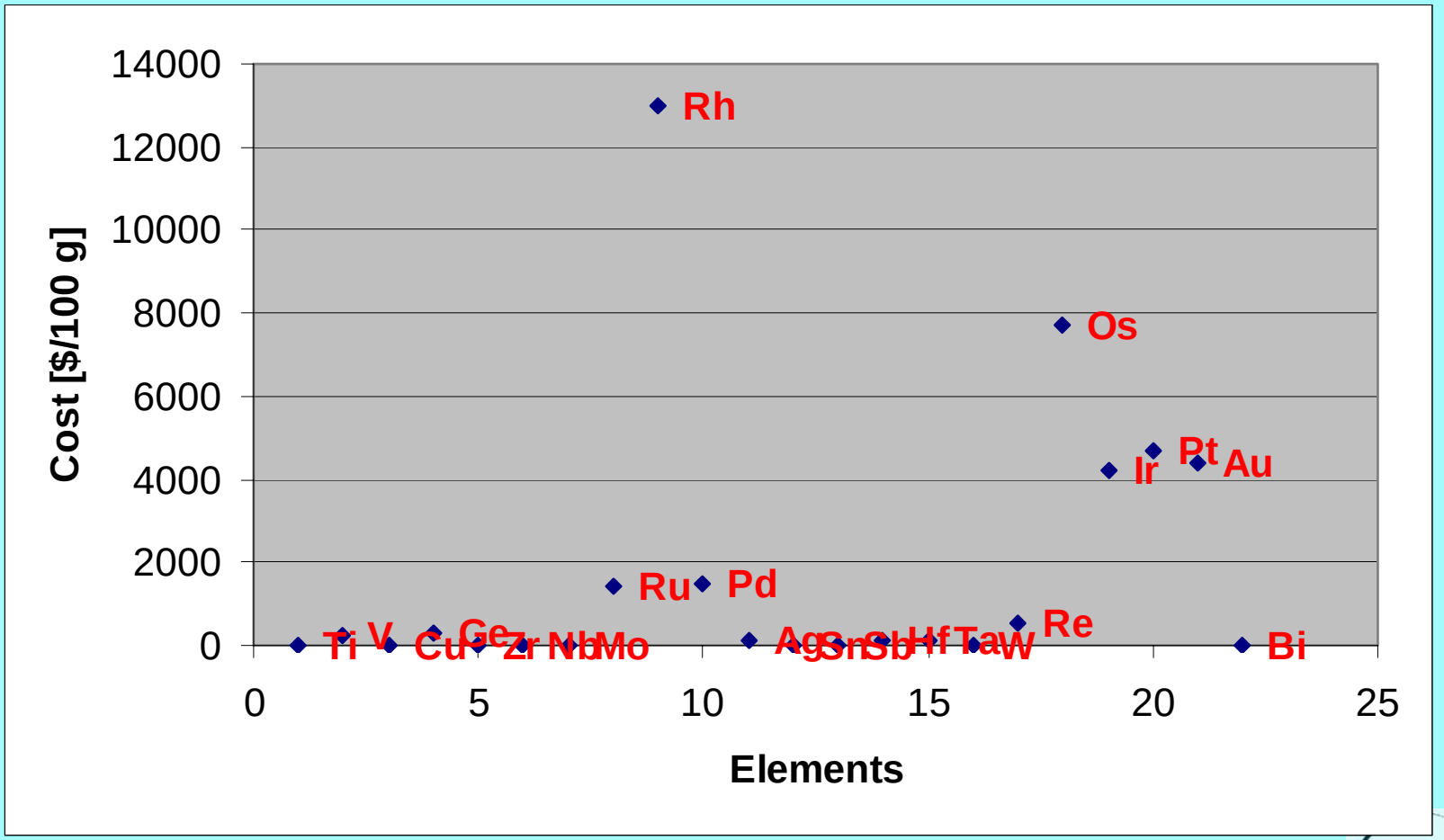
Highly oxophillic, soluble oxides, poison to PEM

Oxides susceptible to corrosion



SUPERIOR MicroPowders

Further Down Selection: Cost of Raw Materials



SUPERIOR MicroPowders

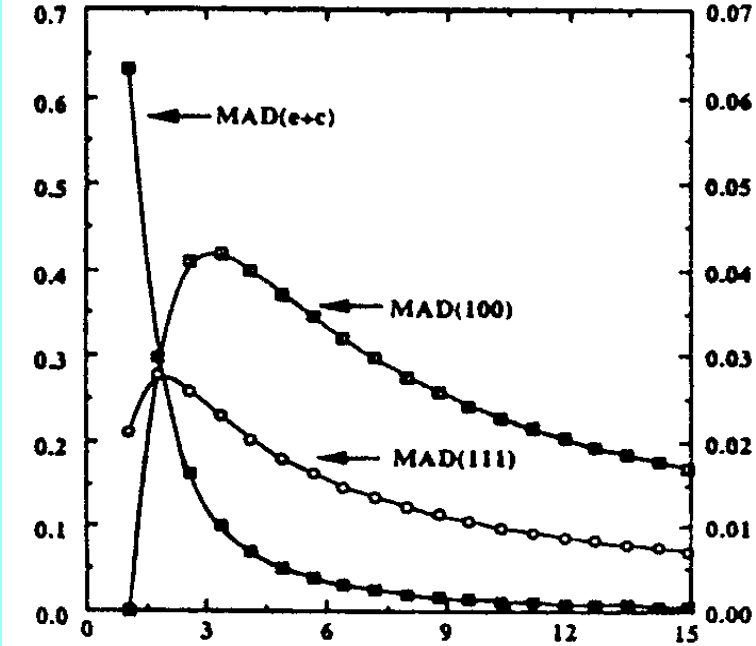
Further Selection Refinement: Activity in ORR

- Role of electronic and geometric parameters
  - » d-band vacancy; % d character, latent heat of sublimation, heat of adsorption, strength of adsorption bond (M-O)
  - » crystal structure; interatomic distance, crystallite size, defects
- Two main trends in dependence of electrochemical performance as function of physicochemical property:
  - » "volcano" type - current density v.s M-O bond strength, latent heat of sublimation, d-band vacancies of electrode metal, % d-character
  - » linear type - specific activity vs. nearest -neighbor distance
- Particle-size effects
  - » change in concentration of various crystallographic sites with change in particle size

Reference: K. Kinoshita, "Electrochemical Oxygen Technology", J. Whiley&Sons, 1992

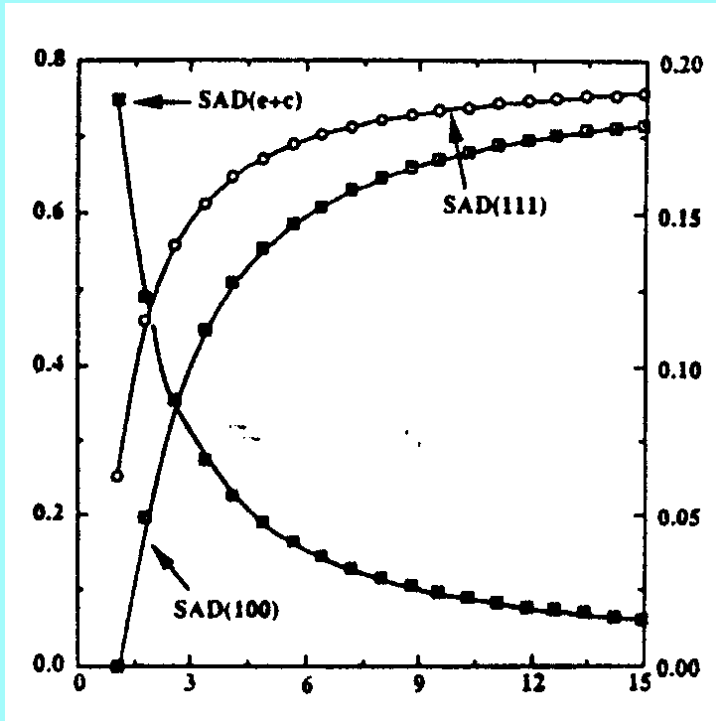
Examples of Particle Size Effects

Mass-averaged distribution for MAD (111), MAD (e-c)



Particle size (nm)

Surface-averaged distribution for SAD (111), SAD (e-c)



SAD (100)

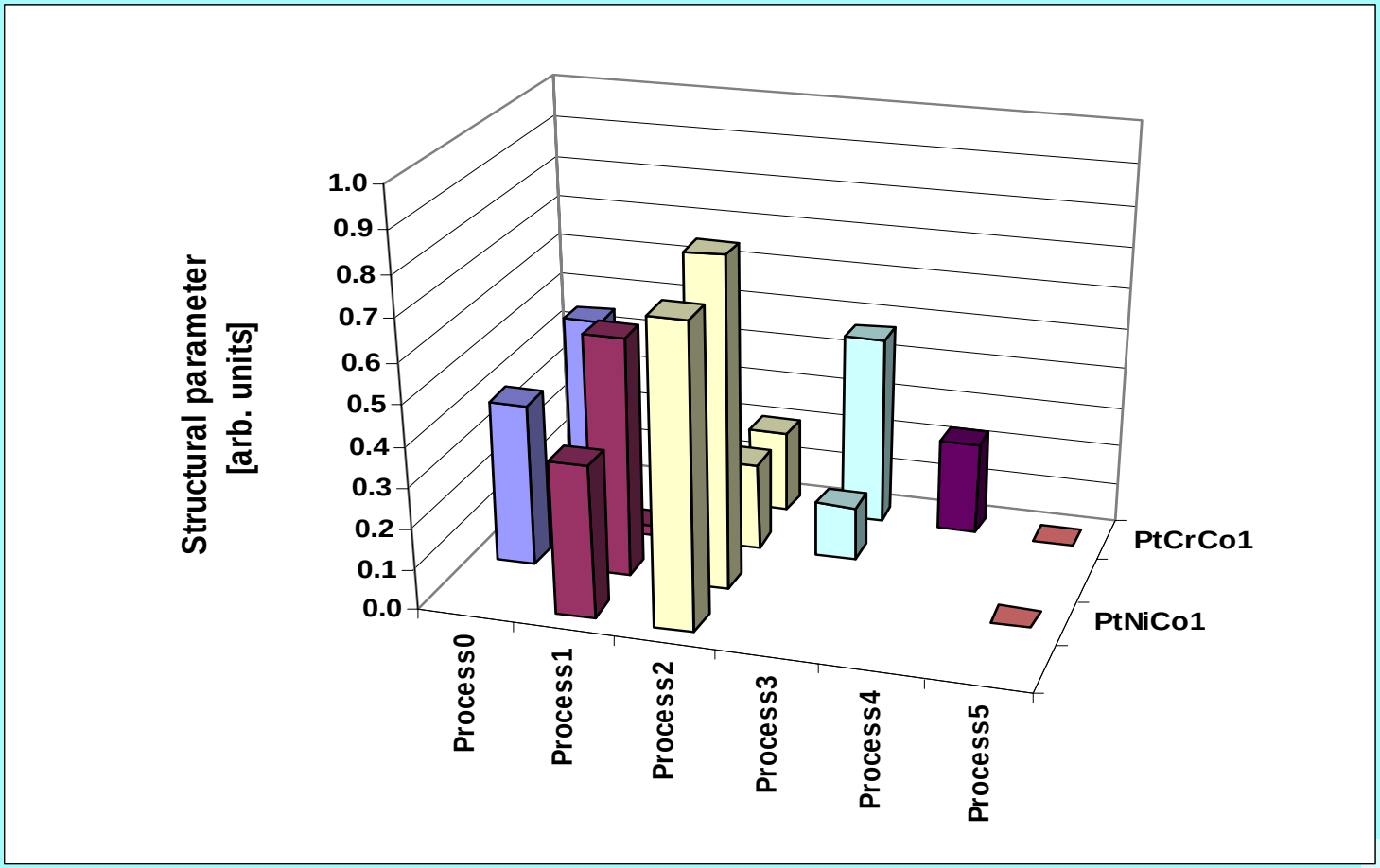
Particle size (nm)

SUPERIOR MicroPowders

Synthesis of Pt and Pt-alloys Electrocatalysts

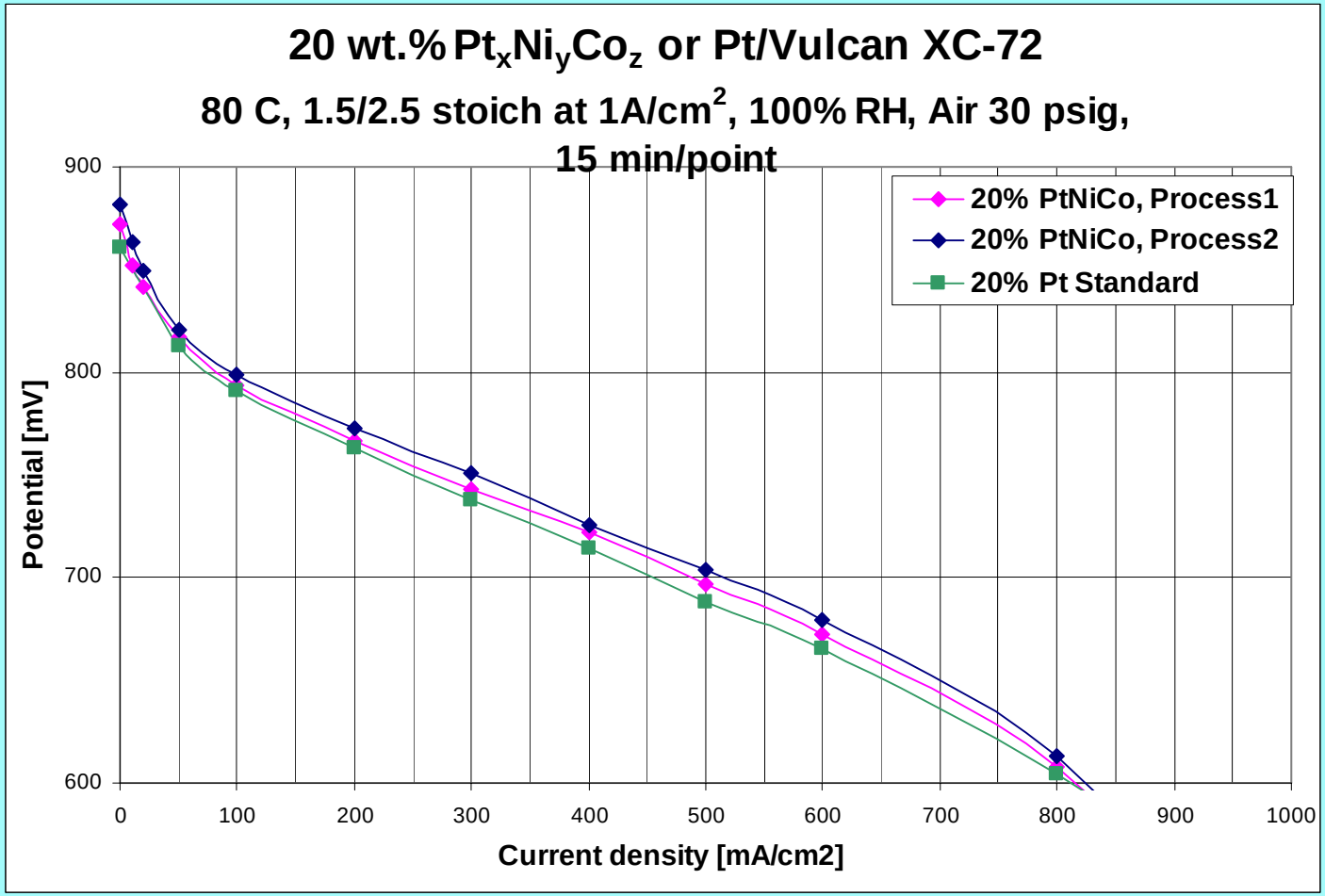
- Pt precursor development to ensure compatibility with various other precursors used for alloys
- Optimization of active phase loadings and type of carbon support
  - » 5, 10, 20, 30 wt.% Pt/SB
  - » 60 wt.% Pt/C (high surface area support)
- Synthesis of selected binary and ternary alloys
  - » binary - Pt_xCo_y; Pt_xPd_y; Pt_xCr_y; Pt_xRu_y;
  - » ternary - $Pt_xNi_yCo_z$; $Pt_xCr_yCo_z$;
- XRD used as a primary screen for degree of alloying and dispersion of active phase

Synthesis of Ternary Pt-alloys Electrocatalysts



SUPERIOR MicroPowders

Performance of Ternary Pt-alloys Electrocatalysts



0.25 mgM/cm² total loading

Nafion 112

20 wt.%Pt/C

4.2 gPt/kW

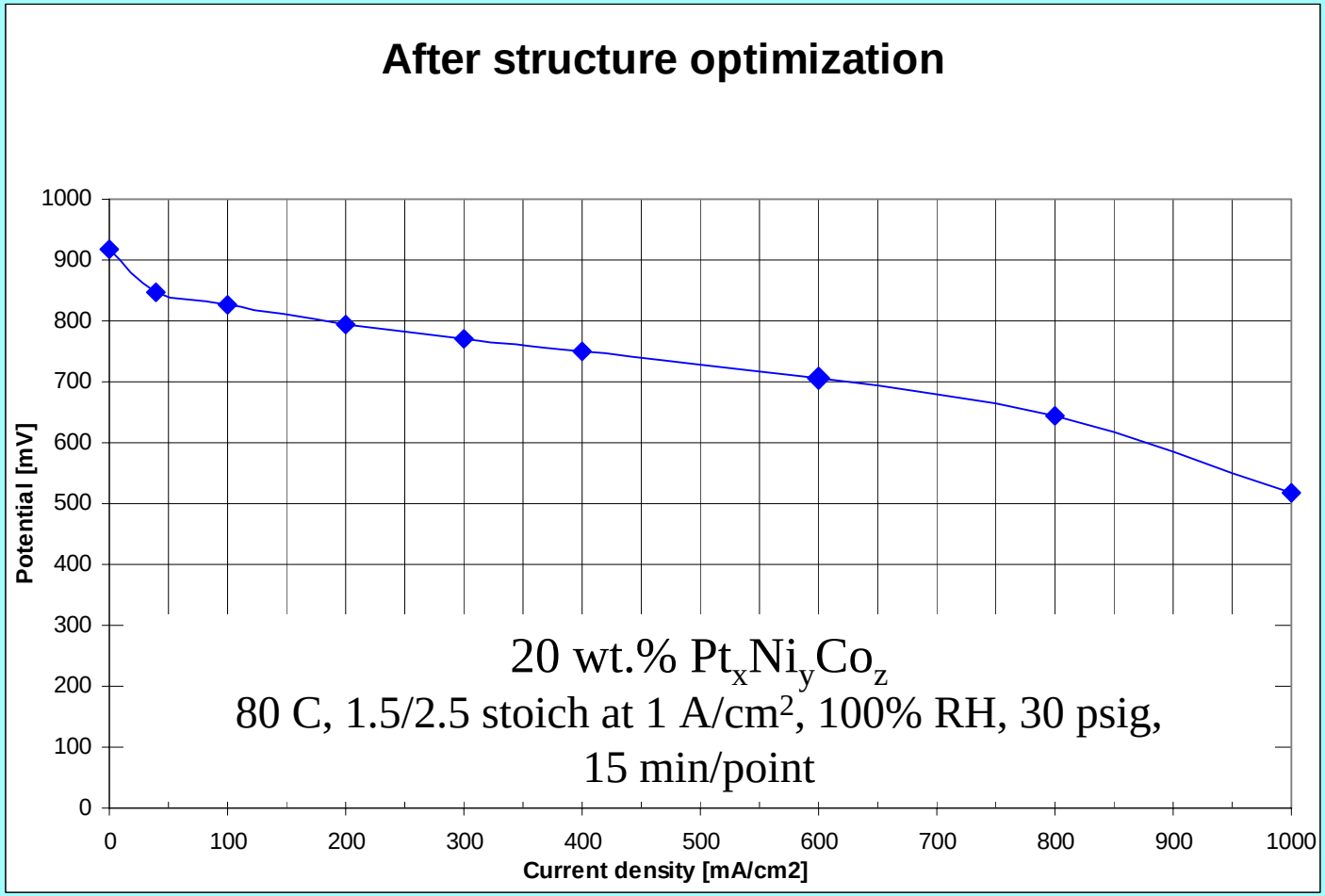
20 wt.% $Pt_xNi_yCo_z$/C

2.6 gPt/kW

40 % improvement vs. Pt/C

SUPERIOR MicroPowders

Performance of Ternary Pt-alloys Electrocatalysts



0.25 mgM/cm² total loading

Nafion 112

20 wt.% $Pt_xNi_yCo_z$/C

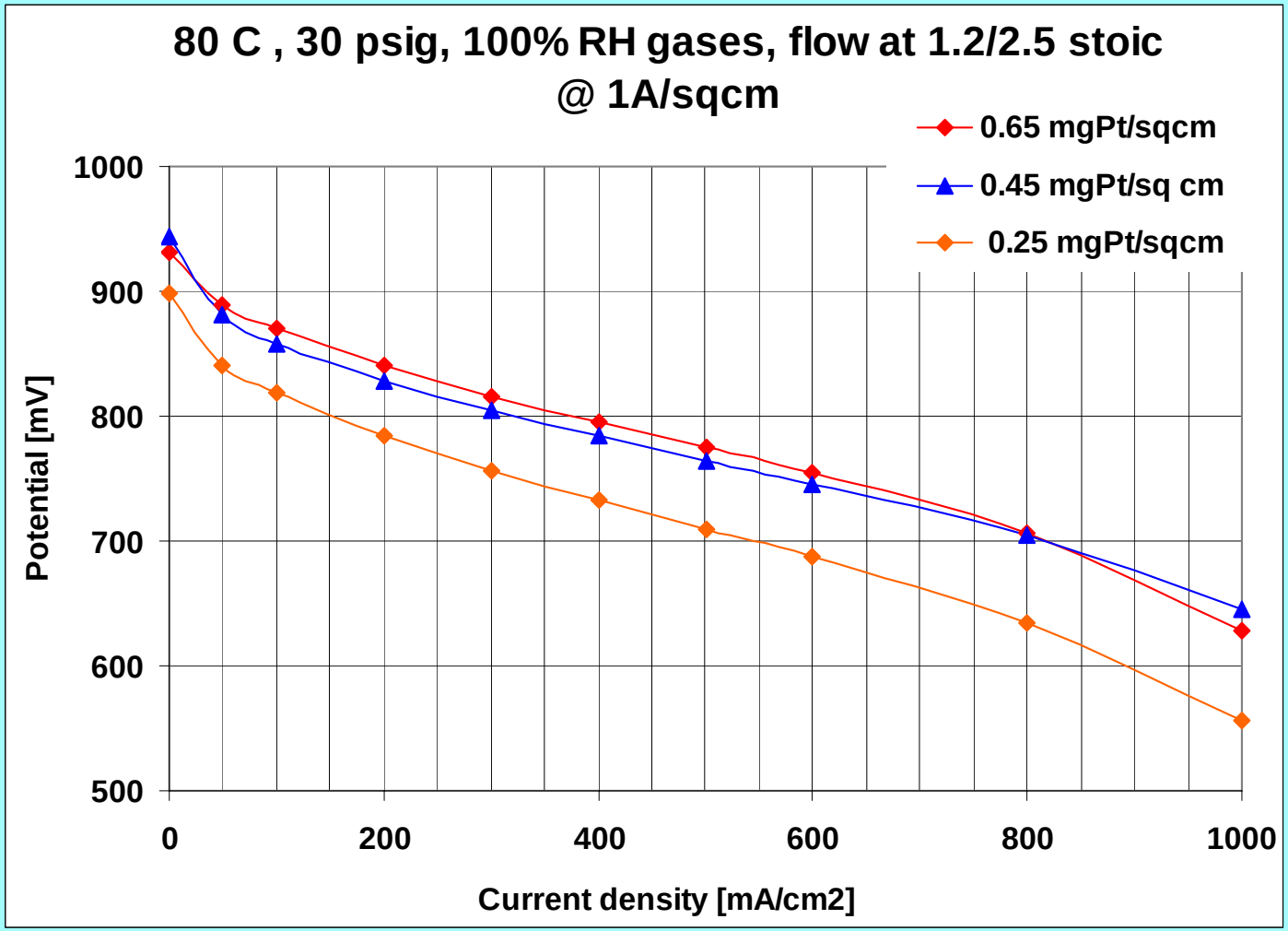
1.5 gPt/kW

SUPERIOR MicroPowders

MEA Structure Optimization

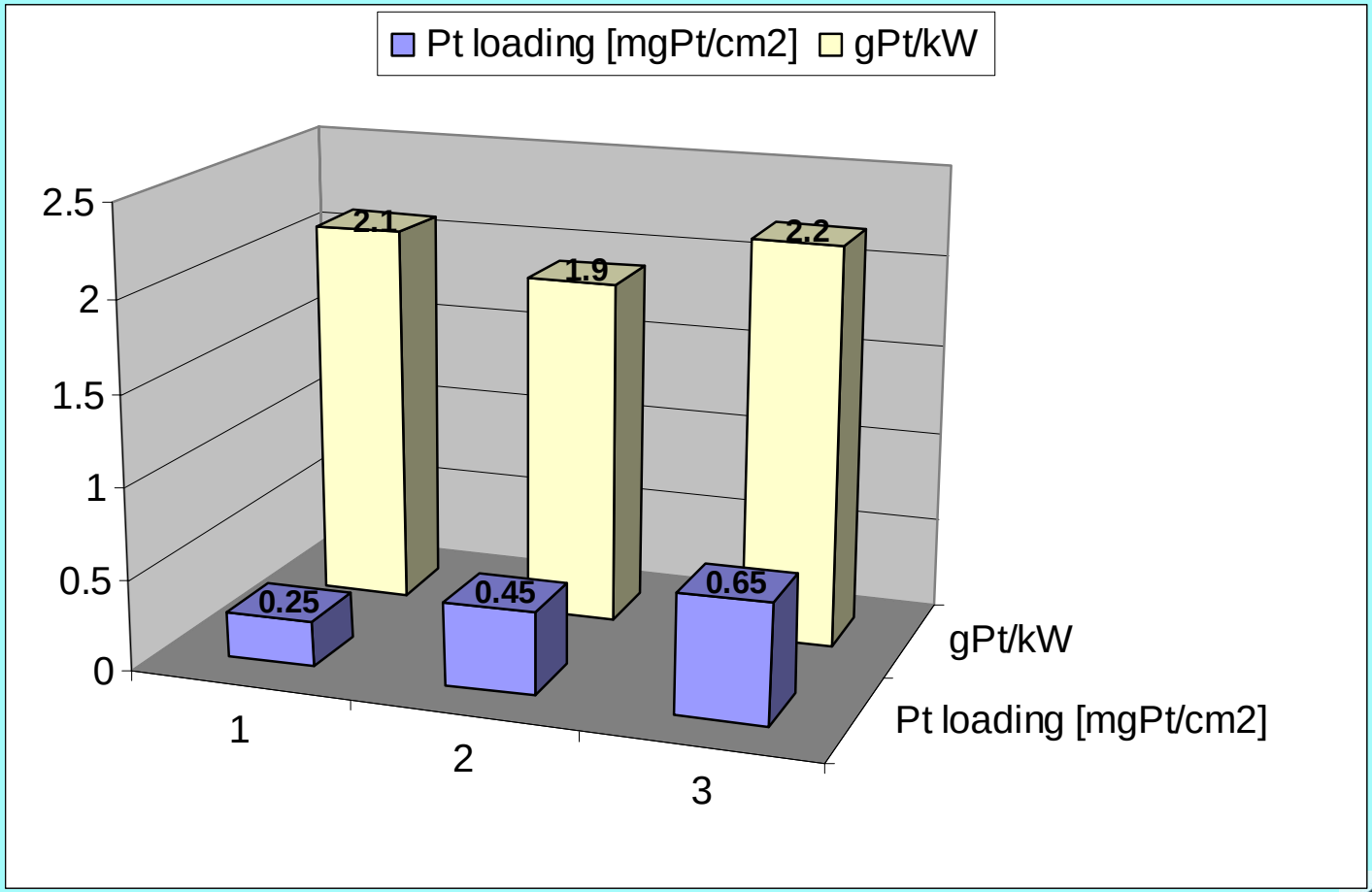
- Optimization of catalyst and ionomer loadings
  - 0.1 - 0.6 mg M/cm^2
  - In combination with various wt.% M/carbon catalysts
- Testing with variations in the:
  - Membrane Nafion 112, Nafion 117, Nafion 1035
  - Catalyst (carbon): Ionomer ratio in the electrode inks
  - GDL type
  - Humidification level for gases
- Electrode deposition technique
  - Method A
  - Method B

Various Catalysts and Pt loadings



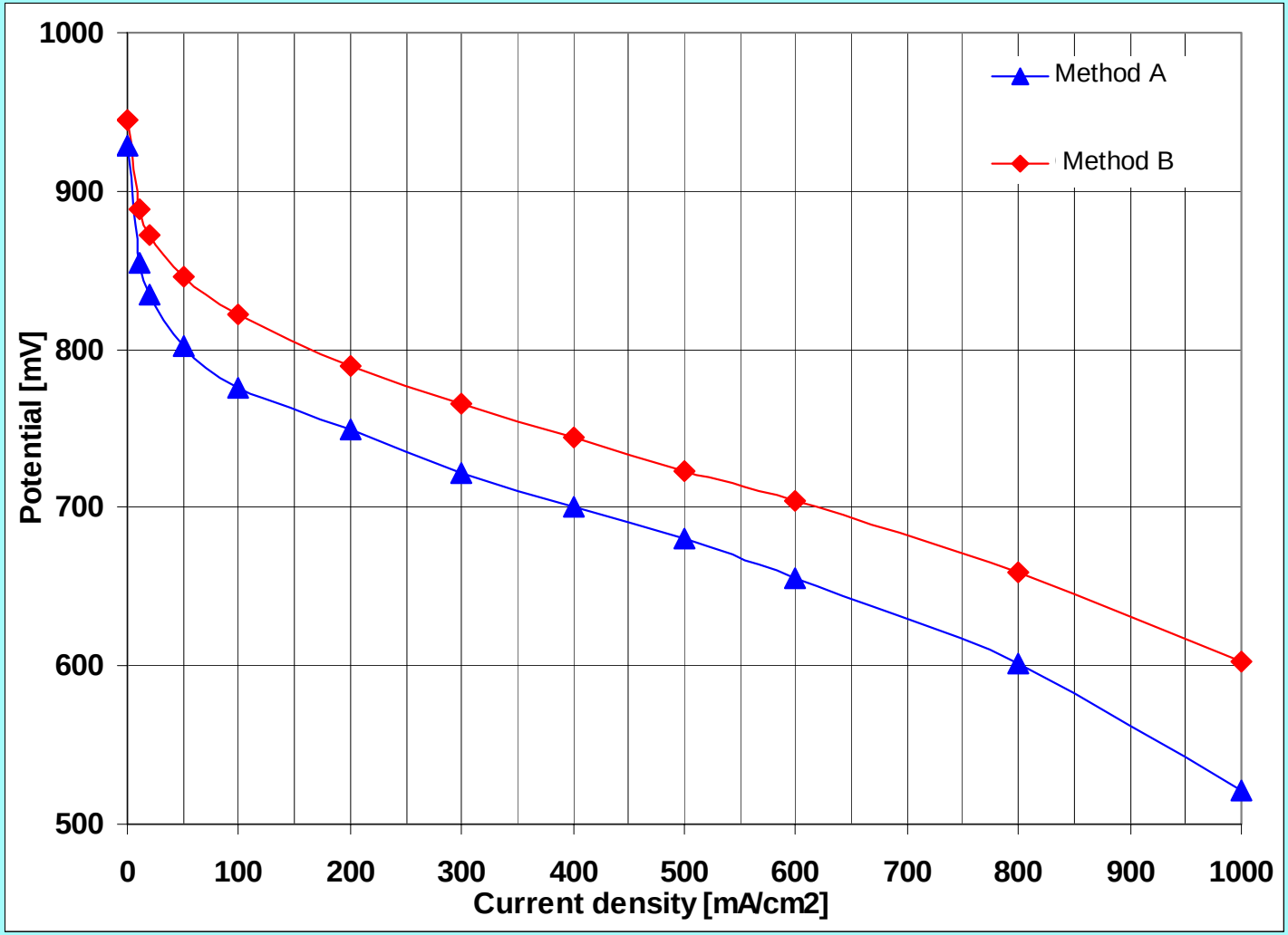
SUPERIOR MicroPowders

Various Catalysts and Pt loadings



SUPERIOR MicroPowders

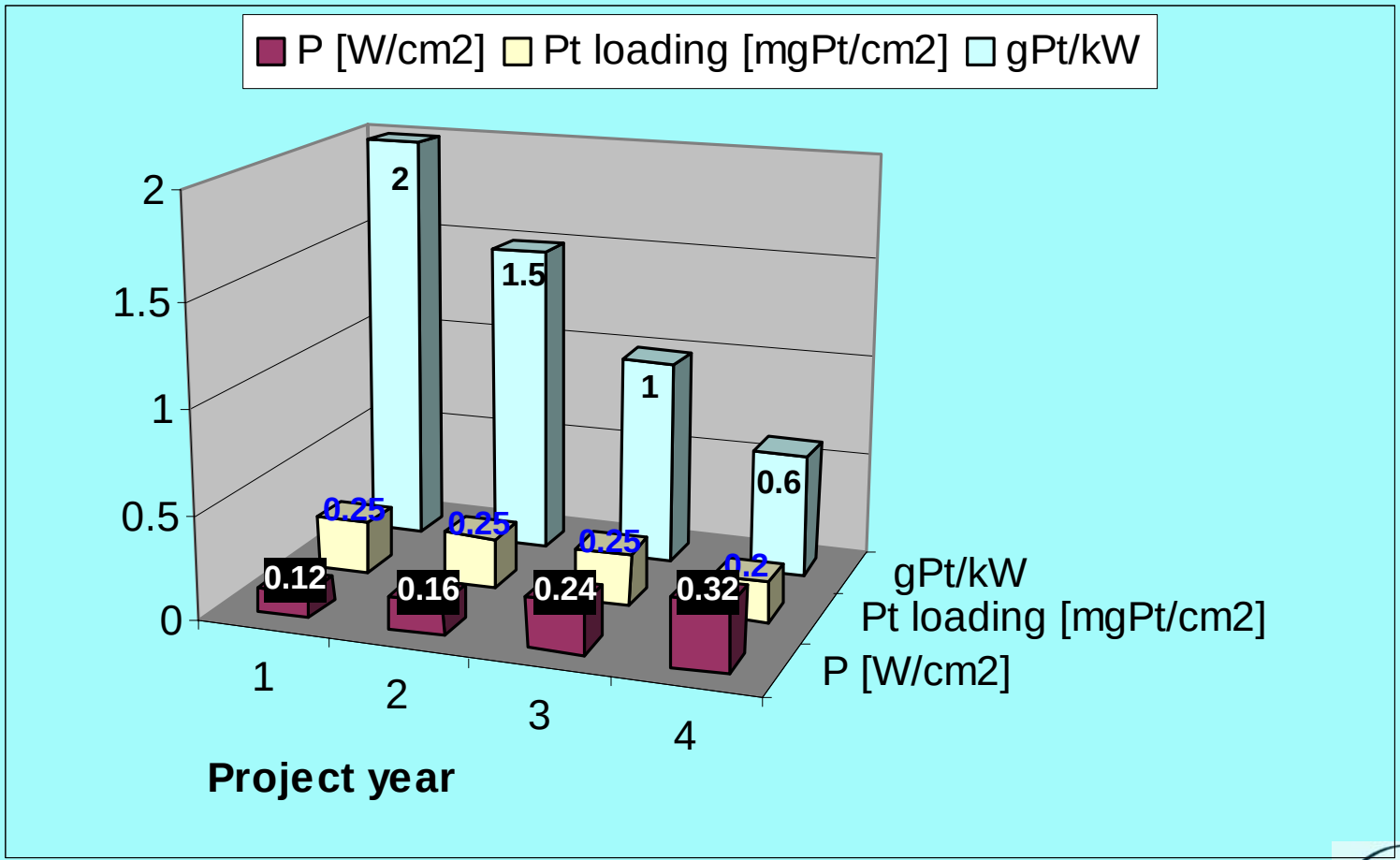
Deposition Method A vs. B



- *0.25 mgPt/cm² total loading*
- *20wt.%Pt/C*
- *Nafion 112*
- *Method A: 6.3 gPt/kW*
- *Current: 1.9 gPt/kW*

SUPERIOR MicroPowders

Performance Targets



SUPERIOR MicroPowders

Accomplishments

- Combinatorial system designed and assembly on schedule
- Rapid screening method in place and benchmarked
- Binary and ternary Pt-Alloy catalysts synthesized and improved performance demonstrated
- Strategy for combinatorial approach in place
- All critical components for combinatorial discovery based on spray pyrolysis approach in place
- Spray-based powder manufacturing offers the best opportunity to reproduce the discovery and scale the commercially useful volumes

SUPERIOR MicroPowders

Acknowledgements

- *DOE OTT, Award DE-FC0402AL67620, Topic 1A1*
- *DOE Program Manager: JoAnn Milliken*
- *SMP for cost share funding*
- *The whole SMP team and especially:*

  Jim Brewster, Jenny Plakio, Heat Quiggle

SUPERIOR MicroPowders